*March* 1, 1883.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

In pursuance of the Statutes, the names of Candidates recommended for election into the Society were read from the Chair, as follows:—

Aitchison, James Edward Tierney, Surgeon-Major, M.D., F.R.C.S., F.R.S.E.
Allman, Professor George Johnston, LL.D.
Baird, A. W., Major R.E.
Baxendell, Joseph, F.R.A.S.
Bell, James, F.I.C.
Browne, James Crichton, M.D., LL.D., F.R.S.E.
Browne, Walter Raleigh, M.A., M.I.C.E.
Buchanan, Professor George, M.A., M.D.
Burdett, Henry Charles, F.L.S., F.S.S.
Colomb, Philip H., Captain R.N.
Creak, Ettrick William, Staff Commander R.N.
Cunningham, Allan Joseph Champneys, Major R.E.
Curtis, Arthur Hill, A.M., LL.D., D.Sc.
Dobson, George Edward, Surgeon-Major, M.A., M.B., F.L.S.
Duncan, James Matthews, A.M., M.D., LL.D.
Fitzgerald, Prof. George Francis, M.A.
Flight, Walter, D.Sc., F.G.S.
Foster, Professor Balthazar Walter, F.R.C.P.
Frost, Rev. Percival, M.A.
Gill, David, LL.D., F.R.A.S.
Goodeve, Professor Thomas Minchin, M.A.
Groves, Charles Edward, F.C.S.
Grubb, Howard, F.R.A.S.
Herschel, Professor Alexander Stewart.
Hicks, Henry, M.D., F.G.S.
Hudleston, Wilfrid H., M.A., F.G.S., F.C.S.
Kent, William Saville, F.Z.S.
Langley, John Newport, M.A.
McKendrick, John G., M.D.
Meldola, Raphael, F.R.A.S., F.C.S.
Miller, Francis Bowyer, F.C.S.
Milne, Professor John, F.G.S.
Priestley, Professor William Overend, M.D., F.R.C.P.
Pritchard, Urban, M.D., F.R.C.S.
Ransome, Arthur, M.A., M.D.
Reinold, Professor Arnold William, M.A.
Rendel, George Wightwick, M.I.C.E.
Ringer, Professor Sydney, M.D.
Rodwell, George F., F.R.A.S., F.C.S.
Sanders, Alfred, M.R.C.S., F.L.S.
Tenison-Woods, Rev. Julian E., M.A., F.L.S., F.G.S.
Tidy, Professor Charles Meymott, M.B., F.C.S.
Tribe, Alfred, F.C.S.
Trimen, Roland, F.L.S., F.Z.S.
Venn, John, M.A.

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Walker, John James, M.A.
Warren, Charles, C.M.G., Major R.E.
Watson, Professor Morrison, M.D.
Williams, Charles Theodore, M.A., M.D., F.R.C.P.

The following Paper was read:—

I. "Contributions to the Chemistry of Storage Batteries." By E. FRANKLAND, D.C.L., F.R.S. Received February 21, 1883.

1. *Chemical Reactions.*—The chemical changes occurring during the charging and discharging of storage batteries have been the subject of considerable difference of opinion amongst chemists and physicists. Some writers believe that much of the storage effect depends upon the occlusion of oxygen and hydrogen gases by the positive and negative plates or by the active material thereon, some contend that lead sulphate plays an important part, whilst others assert that no chemical change of this sulphate occurs either in the charging or discharging of the plates.

To test the first of these opinions, I made two plates of strips of thin lead twisted into corkscrew form, and after filling the gutter of the screw with minium, so as to form a cylinder that could be afterwards introduced into a piece of combustion-tubing, these plates were immersed in dilute sulphuric acid and charged by the dynamo-current in the usual manner. The charging was continued until the whole of the minium on the + and — plates respectively was converted into lead peroxide and spongy lead, and until gas bubbles streamed from the pores of the two cylinders.

After removal from the acid the plates were superficially dried by filter-paper, and immediately introduced into separate pieces of combustion-tubing previously drawn out at one end, so as to form gas delivery tubes. The wide ends of these tubes were then sealed before the blowpipe, care being taken not to allow the heat to reach the enclosed cylinders. The tube containing the cylinder of reduced lead was now gradually heated until the lead melted, the drawn-out end of the tube meanwhile dipping into a pneumatic trough. The gas expelled from the tube consisted almost exclusively of the expanded air of the tube and contained mere traces of hydrogen.

The tube containing the cylinder of lead peroxide was similarly treated, except that the heat was not carried high enough to decompose the peroxide. Mere traces, if any, of occluded oxygen were evolved.

These results justify the conclusion that occluded gases play, practically, no part in the phenomena of the storage cell.

With regard to the function of lead sulphate in storage batteries,

I have observed that during the so-called "formation" of a storage cell, a very large amount of sulphuric acid disappears from the liquid contents of the cell: indeed sometimes the whole of it is withdrawn. The acid so removed must be employed in the formation of insoluble lead sulphate upon the plates which, in fact, soon become coated with a white deposit of the salt, formed equally upon both positive and negative surfaces. This visible deposit is, however, very superficial, and does not account for more than a very small fraction of the acid which actually disappears from solution. The great bulk of the lead sulphate cannot be discovered by the eye, owing to its admixture with chocolate-coloured lead peroxide.

Unless the coated plates have been previously immersed for several days in dilute sulphuric acid, this disappearance of acid during their "formation" continues for ten or twelve days. At length, however, as the charging goes on, the strength of the acid ceases to diminish and soon afterwards begins to augment. The increase continues until the maximum charge has been reached and abundance of oxygen and hydrogen gases begin to be discharged from the plates; that is to say, until the current is occupied exclusively, or nearly so, in the electrolysis of hexabasic sulphuric acid expressed by Burgoin in the following equation:—

| | | Eliminated on + plate. | | Eliminated on − plate. |
|---|---|---|---|---|
| $SO_6H_6$ | = | $SO_3$ | + $3O$ | + $3H_2$. |
| Sulphuric acid. | | Sulphuric anhydride. | | |

Of course the sulphuric anhydride immediately combines with water and regenerates hexabasic sulphuric acid:—

$$SO_3 + 3OH_2 = SO_6H_6.$$

On discharging the cell, the specific gravity of the acid continually decreases until the discharge is finished, when it is found to have sunk to about the same point from which it began to increase during the charging. Hence it is evident that, during the discharge, the lead sulphate, which was continuously decomposed in charging, was continuously reformed in discharging.

The chief if not the only chemical changes occurring during the charging of a storage battery, therefore, appear to be the following:—

1st. The electrolysis of hexabasic sulphuric acid according to the equation already given.

2nd. The reconversion of sulphuric anhydride into sulphuric acid.

3rd. The chemical action on the coating of the + plate.

| | | | | | | |
|---|---|---|---|---|---|---|
| $SO_4Pb$ | + | $O + 3OH_2$ | = | $PbO_2$ | + | $SO_6H_6$. |
| Lead sulphate. | | | | Lead peroxide. | | Hexabasic sulphuric acid. |

4th. The chemical action on the coating of the negative plate :—

$$\underset{\text{Lead sulphate.}}{SO_4Pb} + H_2 + 2OH_2 = Pb + \underset{\text{Hexabasic sulphuric acid.}}{SO_6H_6}.$$

If I have correctly described these changes, the initial action in the charging of a storage cell is the electrolysis of hexabasic sulphuric acid, each molecule of which throws upon the positive plate three atoms of oxygen, and upon the negative plate six atoms or three molecules of hydrogen. Each atom of oxygen decomposes one molecule of lead sulphate on the positive plate, producing one molecule of lead peroxide, and one of sulphuric anhydride, the latter instantly uniting with three molecules of water to form hexabasic sulphuric acid.

The following are the chemical changes which I conceive to occur during the discharge of a storage cell :—

1st. The electrolysis of hexabasic sulphuric acid as in charging.

2nd. The reconversion of sulphuric anhydride into hexabasic sulphuric acid as already described.

3rd. The chemical action upon the coating of what was before the positive plate or electrode, but which now becomes the negative plate of the cell, that is to say, the plate from which the positive current issues to the external circuit :—

$$\underset{\text{Lead peroxide.}}{PbO_2} + H_2 = \underset{\text{Lead oxide.}}{PbO} + \underset{\text{Water.}}{OH_2}.$$

The lead oxide thus formed is immediately converted into lead sulphate :—

$$PbO + SO_6H_6 = SO_4Pb + 3OH_2.$$

4th. The chemical action upon the coating of what has now become the positive plate of the cell :—

$$Pb + O + SO_6H_6 = SO_4Pb + 3OH_2.$$

Thus in discharging, as in charging, a storage cell, the initial action is the electrolysis of hexabasic sulphuric acid. The oxygen eliminated on the positive plate reconverts the reduced metal of that plate into lead oxide, whilst the hydrogen transforms the lead peroxide on the negative plate into the same oxide, which in both cases is immediately converted into lead sulphate by the surrounding sulphuric acid, thus restoring both plates to their original condition before the charging began.

The real "formation" of the cell consists, I conceive, in the more or less thorough decomposition of those portions of the lead sulphate which are comparatively remote from the conducting metallic nucleus of the plate. Lead sulphate itself has a very low conductivity, whilst lead peroxide, and especially spongy lead, offer comparatively little

resistance to the current, which is thus enabled to bring the outlying portions of the coating under its influence. It may be objected that, during the discharge, the work of formation would be undone; but probably, in the ordinary use of a storage battery, the discharge is never completed. Thus I have found that, in a small cell containing two plates $6'' \times 2''$, short circuiting with a thick copper wire for twelve hours was far from producing complete discharge, for on breaking this short circuit, the cell *instantly* rang violently an electric bell with which it was previously connected. In ordinary discharges of "formed" cells, therefore, the lead sulphate on the positive and negative plates still remains mixed with sufficient lead oxide and spongy lead respectively to give it a higher conducting power than the sulphate alone possesses.

2. *Chemical Estimation of the Charge in a Storage Cell.*—No method has hitherto been known by which the charge in a storage cell could be ascertained without discharging the cell; but the results of the foregoing experiments indicate a very simple means of ascertaining the amount of stored energy without any interference with the charge itself. The specific gravity and consequent strength of the dilute sulphuric acid of a "formed" cell being known in its uncharged and also in its fully charged condition, it is only necessary to take the specific gravity of the acid at any time in order to ascertain the proportion of its full charge which the cell contains at that moment; and if the duty of the cell is known, the amount of energy stored will also be thereby indicated. In the case of the cell with which I have experimented, containing about seven quarts of dilute sulphuric acid, each increase of ·005 in the specific gravity of the dilute acid means a storage of energy equal to 20 ampères of current for one hour, obtainable on discharge.

I hope shortly to be able to express, in terms of current from the cell, the definite relation between the amount of energy stored and the weight of sulphuric acid liberated.